

Hydrogenation of carboxylic acids or anhydrides or esters thereof to give alcohols

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Description

The invention relates to a process for increasing the catalytic activity and avoiding secondary reactions in the hydrogenation of  
10 carboxylic acids or derivatives thereof by adding specific basic alkali metal compounds or alkaline earth metal compounds to the hydrogenation feed.

It is known to use basic components during the preparation of  
15 hydrogenation catalysts. A certain amount of these components is then still present on the finished catalyst. For example, EP-A 528 305 describes the preparation of a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst in which basic compounds, such as alkali metal carbonates, alkali metal hydroxides or alkali metal hydrogencarbonates, are used  
20 during precipitation of the catalyst constituents. A small amount of the alkali metal additive then remains in the catalyst. Another example of preparing alkali metal-containing catalysts is described in DE-A 2 321 101, in which Co-containing catalysts are prepared. EP-A 552 463 describes the preparation of Cu/Mn/Al  
25 catalysts which, owing to their preparation, may likewise contain small amounts of alkali metal.

The resulting hydrogenation catalysts contain the alkali metal uniformly distributed throughout the whole catalyst composition.  
30 However, since only the outer or accessible surface of the catalyst is catalytically active, the amount of alkali metal at these sites is very small and is generally washed out quickly by the stream to be hydrogenated since the alkali metal is not bonded covalently, but is present only in a loosely bonded form.  
35 In addition, the introduction of compounds which are able to acidify the catalyst rapidly exhausts the capacity of the basic centers produced by the alkali metal. As a result, reactions which are promoted by acid catalysis, such as etherifications or dehydrations, may lessen the selectivity of hydrogenation to  
40 alcohols. In general, the introduction of compounds which acidify the catalyst sometimes severely shortens the service life of the catalyst since the structure of the catalyst surface changes, for example as a result of catalyst constituents being washed out or recrystallization of the active metals.

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Accordingly, the hydrogenation catalysts are sometimes sensitive to the hydrogenation feed itself or to impurities which are present in the hydrogen used or in the hydrogenation feed. Thus, many catalysts in the hydrogenation of carboxylic acids are, for example, not only acidified, but also severely damaged chemically as a result of catalyst components being washed out. Even if the feed material does not contain any carboxylic acids, but, for example, contains esters, the carboxylic acids are usually liberated by hydrolysis of the esters by traces of water. Another problem concerns impurities, for example organic halogen compounds, which may be introduced into the hydrogenation, for example with the hydrogen, and have adverse effects even when the contents of these substances are below 1 ppm. Thus, it is known that, for example, Cu catalysts can be used to remove traces of halogen from feed streams by chemisorption (US 5,614,644). Without such a preabsorption, the halogen is absorbed on the hydrogenation catalyst, where it leads firstly to acidification and secondly to structural modifications of the catalyst. Accordingly, the technical solution to the problem described typically involved the upstream installation of a "guard bed", in which undesired impurities were absorbed. This cannot of course remove the acids involved in the reaction, such as the carboxylic acids which form or are used as hydrogenation feed.

It is an object of the present invention to propose a process by means of which the catalyst-impairing effect of the acids involved in the reaction and also of the impurities introduced can be reduced or eliminated.

We have found that this object is achieved by a process for the catalytic hydrogenation of carboxylic acids or anhydrides or esters thereof to alcohols on heterogeneous catalysts which comprise or consist of hydrogenating elements from groups 6, 7, 8, 9, 10 and 11 and, where appropriate, from groups 2, 14 and 15 of the Periodic Table of the Elements, in the liquid phase at from 100 to 300°C and from 10 to 300 bar, which comprises adding from 1 to 3000 ppm, in particular from 3 to 1000, preferably from 5 to 600 ppm, based on the liquid hydrogenation feed, of a basic alkali metal compound or alkaline earth metal compound selected from the group consisting of hydroxides, carbonates, carboxylates and alkoxides to the hydrogenation reaction mixture.

DE 1 235 879, Example 16, discloses the addition of trisodium phosphate to the hydrogenation feed. This example describes the hydrogenation of a carboxylic acid mixture which comprises 0.1% by weight of  $\text{Na}_3\text{PO}_4$ , inter alia adipic acid, glutaric acid,

succinic acid and 6-hydroxycaproic acid, a carboxyl acid mixture which has already been hydrogenated, and also an undefined amount of "crude monoalcohols" whose water content has been adjusted to 7%. The sole addition of  $\text{Na}_3\text{PO}_4$  to the hydrogenation feed is not, however, a suitable measure for increasing the catalyst activity and service life. After a short time in the presence of acidifying constituents in the reaction mixture there is a drastic drop in activity.

- 10 Carboxylic acids and derivatives may be carboxylic acids themselves and esters, and also internal esters, i.e. lactones, and anhydrides thereof. Examples thereof are acetic esters, propionic esters, hexanoic esters, dodecanoic esters, pentadecanoic esters, hexadecanoic esters,
- 15 2-cyclododecylpropionic esters, esters of glycerol with fatty acids, maleic diesters, succinic diesters, fumaric diesters, glutaric diesters, dimethyl adipates, 6-hydroxycaproic esters, cyclohexanedicarboxylic diesters, benzoic esters, butyrolactone, caprolactone, maleic acid, succinic acid, itaconic acid, adipic
- 20 acid, 6-hydroxycaproic acid, cyclohexanedicarboxylic acid, benzoic acid, maleic anhydride and succinic anhydride. Preferred starting materials are diesters, in particular diesters of low molecular weight alcohols with dicarboxylic acids having from 4 to 6 carbon atoms.
- 25 Suitable basic compounds are especially alkali metal hydroxides and alkaline earth metal hydroxides, such as  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{RbOH}$ ,  $\text{CsOH}$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$  or  $\text{Ba}(\text{OH})_2$ . The alkali metals or alkaline earth metals may also be in the form of carboxylates,
- 30 e.g. as formate, acetate, propionate, maleate or glutarate, or as alkoxides, such as methoxide, ethoxide or propoxide. Carbonates are also suitable. The basic compounds should always dissolve homogeneously in the hydrogenation feed. If this cannot be ensured, it is also possible to introduce the basic compound in a
- 35 suitable solvent as a separate stream into the hydrogenation itself or into the hydrogenation feed. The amounts of alkali metal or alkaline earth metal, based on the hydrogenation stream, are very low, being between 1 and 3000 ppm, preferably between 3 and 1000 ppm, particularly preferably between 5 and 600 ppm.
- 40 The basic component is preferably introduced continuously. Batchwise addition is, however, also possible. Within a short time, it is also possible for greater amounts of basic components than 3000 ppm, based on the hydrogenation feed, to enter the hydrogenation. On average, the amounts are, however, below
- 45 3000 ppm.

It is surprising that even after prolonged addition of the basic components, there are no deposits on the catalyst.

The hydrogenation takes place in the liquid phase. It is not important whether, in the case of fixed-bed catalysts, an upward or downward flow method is chosen. Hydrogenation using suspended catalysts is also possible.

The hydrogenation catalysts which may be used in the novel process are generally heterogeneous catalysts suitable for the hydrogenation of carbonyl groups. Examples thereof are described, for example, in Houben-Weyl, Methoden der Organischen Chemie, Volume IV/1c, pp. 16 to 26.

Of these hydrogenation catalysts, preference is given to those which comprise one or more elements from groups 6, 7, 8, 9, 10 and 11 and, where appropriate, from groups 2, 14 and 15 of the Periodic Table of the Elements, in particular copper, chromium, rhenium, cobalt, rhodium, nickel, palladium, iron, platinum, indium, tin and antimony. Particular preference is given to catalysts which comprise copper, cobalt, palladium, platinum or rhenium.

Suitable catalysts are especially unsupported catalysts. In the great majority of cases, the catalytically active metals are not on carrier materials. Examples thereof are Raney catalysts, e.g. based on Ni, Cu or cobalt. Other examples are Pd black, Pt black, Cu sponge, or alloys or mixtures of, for example, Pd/Re, Pt/Re, Pd/Ni, Pd/Co or Pd/Re/Ag.

The catalysts employed in the novel process may also be, for example, precipitated catalysts. Catalysts of this type can be prepared by precipitating their catalytically active components from solutions of salts thereof, in particular from solutions of their nitrates and/or acetates, for example by adding solutions of alkali metal hydroxide and/or alkaline earth metal hydroxide and/or alkali metal carbonate and/or alkaline earth metal carbonate, e.g. as sparingly soluble hydroxides, oxide hydrates, basic salts or carbonates, then drying the resulting precipitates and subsequently converting them by calcination at, in general, from 300 to 700°C, in particular from 400 to 600°C, into the corresponding oxides, mixed oxides and/or mixed valency oxides, which are reduced, and converted into the actual catalytically active form by treatment with hydrogen or hydrogen-containing gases, generally at from 50 to 700°C, in particular from 100 to 400°C, to give the corresponding metals and/or oxides in a lower

oxidation state. This reduction is generally continued until water is no longer formed. To prepare precipitated catalysts comprising a carrier material, the catalytically active components can be precipitated in the presence of the corresponding carrier material. However, it is also advantageous for the catalytically active components to be precipitated simultaneously with the carrier material from the relevant salt solutions. Preferred hydrogenation catalysts in the novel process are those comprising the hydrogenation-catalyzing metals or metal compounds deposited on a carrier material. Apart from the abovementioned precipitated catalysts, which also comprise a carrier material in addition to the catalytically active components, suitable supported catalysts for the novel process are, in general, those in which the components catalyzing the hydrogenation have been applied to a carrier material, for example by impregnation.

The way in which the catalytically active metals are applied to the carrier is generally not critical and can be brought about in various ways. The catalytically active metals can be applied to these carrier materials by for example impregnation with solutions or suspensions of the salts or oxides of the corresponding elements, drying and subsequent reduction of the metal compounds to the corresponding metals or compounds in a lower oxidation state by means of a reducing agent, preferably using hydrogen or complex hydrides. Another potential way of applying the catalytically active metals to these carriers consists in impregnating the carriers with solutions of salts which readily undergo thermal decomposition, e.g. with nitrates, or complex compounds which readily undergo thermal decomposition, e.g. carbonyl or hydrido complexes of the catalytically active metals, and heating the carrier impregnated in this way to from 300 to 600°C for thermal decomposition of the adsorbed metal compounds. This thermal decomposition is preferably carried out under a protective gas atmosphere. Examples of suitable protective gases are nitrogen, carbon dioxide, hydrogen and the inert gases. The catalytically active metals can furthermore be deposited on the catalyst carrier by vapor deposition or by flame spraying. The content of the catalytically active metals in these supported catalysts is in principle not critical for the success of the novel process. However, higher contents of catalytically active metals generally result in higher space-time conversions than lower contents. In general, the supported catalysts used comprise from 0.1 to 90% by weight, preferably from 0.5 to 40% by weight, of catalytically active metals, based on the entire catalyst. Since these contents refer to the entire catalyst including carrier material, but the different carrier materials have very



different specific gravities and specific surface areas, lower or higher contents than these are also possible without this having a disadvantageous effect on the result of the novel process. It is, of course, also possible to apply a plurality of catalytically active metals to the particular carrier material. Furthermore, the catalytically active metals can be applied to the carrier by for example the process of DE-A 2 519 817, EP-A 1 477 219 and EP-A 285 420. The catalytically active metals are present in the catalysts disclosed in the abovementioned publications as alloys which are produced by thermal treatment and/or reduction after, for example, impregnation with a salt or complex of the abovementioned metals.

Activation both of the precipitated catalysts and of the supported catalysts can also take place in situ at the start of the reaction by the hydrogen which is present, but these catalysts are preferably activated separately before being used.

Suitable carrier materials are generally the oxides of aluminum and titanium, zirconium dioxide, silicon dioxide, clays, such as montmorillonites, silicates, such as magnesium or aluminum silicates, zeolites, such as ZSM-5 or ZSM-10 zeolites, and activated carbon. Preferred carrier materials are aluminum oxides, titanium dioxides, silicon dioxide, zirconium dioxide and activated carbon. It is, of course, also possible to use mixtures of various carrier materials as carrier for heterogeneous catalysts which can be used in the novel process. Examples of heterogeneous catalysts which can be employed in the novel process are the following:

cobalt on activated carbon, cobalt on silicon dioxide, cobalt on aluminum oxide, rhenium on activated carbon, rhenium on silicon dioxide, rhenium/tin on activated carbon, rhenium/platinum on activated carbon, copper on activated carbon, copper/silicon dioxide, copper/aluminum oxide, copper chromite, barium copper chromite, copper/aluminum oxide/manganese oxide, copper/aluminum oxide/zinc oxide, and the catalysts disclosed in DE-A 3 932 332, US-A 3,449,445, EP-A 44 444, EP-A 147 219, DE-A 3 904 083, DE-A 2 321 101, EP-A 415 202, DE-A 2 366 264, EP 0 552 463 and EP-A 100 406.

Preferred catalysts comprise at least one of the metals copper, manganese, cobalt, chromium, palladium, platinum, cobalt or nickel, particularly preferably copper, cobalt, palladium, platinum or rhenium. If only esters are hydrogenated, the hydrogenation catalyst preferably comprises copper.

For the novel process, it is generally not critical which temperature and pressure conditions are used for the

hydrogenation.

The hydrogenation temperature is generally between 100 and 300°C and the hydrogenation pressure is generally between 10 and 300 bar.

By metering the particular basic compounds according to the invention, also in substoichiometric amounts, based on the impurities introduced, it is possible to prevent, or at least severely delay, acidification on the one hand and structural modification of the catalyst on the other. This is evident from an improvement in selectivity, an increase in the useful life of the catalyst, and, in a manner which is not yet fully understood, also by an increase in conversion.

The alcohols obtained in the hydrogenation are desired compounds, e.g. for solvents, intermediates or precursors for plastics such as polyurethanes or polyesters. The novel process is further illustrated in the examples below, but is not limited thereto. The reaction products were analyzed by gas chromatography.

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#### Example 1

About 20 g/h of a 50% ethanolic solution of ethyl 2-cyclododecylidenepropionate (prepared from ethyl 2-bromopropionate and cyclododecane), which also contained 7 ppm of halogen (detected as Cl), were hydrogenated at 220°C/220 bar over 25 ml of a CuO (70%)/ZnO (25%)/Al<sub>2</sub>O<sub>3</sub> (5%) catalyst (precipitation of an aqueous solution of sodium aluminate and zinc(II) nitrite hexahydrate with aqueous sodium carbonate solution, removal of the resulting ZnO- and Al<sub>2</sub>O<sub>3</sub>-containing precipitate by filtration, slurrying of the precipitate with an aqueous solution containing copper(II) nitrate trihydrate and zinc(II) nitrate hexahydrate, precipitation with aqueous sodium carbonate solution, filtration, washing, drying and calcination of the obtained precipitate and shaping of the calcined powder to tablets), which had previously been activated in a stream of hydrogen at 180°C. The content of 2-cyclododecylpropanol (musk odor) in the hydrogenation product was 70% (calculated on an ethanol-free basis). The conversion after about 8 h was about 93% (selectivity 75%). 50 ppm of sodium methoxide were then mixed into the feed stream. As a result, the content of desired product rose to about 77%, and the conversion to 96% (selectivity 80%).

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## Example 2

A mixture (prepared as in DE-A 19 607 953 in the example, steps 1-4) of predominantly dimethyl adipate and methyl 6-hydroxycaproate was hydrogenated (feed 1 kg, reactor temperature 205 to 220°C, pressure 250 bar) over 2.5 l of a T 4489 Cu/Al/Mn catalyst from Süd-Chemie which had previously been activated in a stream of hydrogen at 180°C. The hydrogenation feed contained about 1 ppm of halogen compounds (detected as Cl). At the start of the hydrogenation, the content of the byproduct hexanediol diether present in the hydrogenation product was 0%. After 6 experiment days the ether could be detected. The ether content rose steadily to 0.8% by the 16th experiment day (content of 1,6-hexanediol in the product 27%, residual contents of dimethyl adipate 3.6%, methyl 6-hydroxycaproate 3.2%). 500 ppm of sodium ethoxide, based on the hydrogenation feed, dissolved in methanol, were then introduced into the reactor via a separate feed. Ether was no longer formed (content of 1,6-hexanediol in the product 30%, residual content of dimethyl adipate 1.1%, methyl 6-hydroxycaproate 2.6%).

Whilst operating without addition of Na, the content of Mn in the hydrogenation product was 5 ppm. Whilst metering in Na, the Mn content fell to below 3 ppm.